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Sulfur Tetrafluoride

The Solid-State Structure of SF_4: The Final Piece of the Puzzle**

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Sulfur tetrafluoride is one of the fundamental binary main-group fluorides, and since its discovery in 1929,[1] its structure and chemistry, particularly as a fluorinating agent in organic chemistry, has been the subject of many studies.[2] The structure of SF_4 has been determined in the gas phase by microwave spectroscopy[3] and electron diffraction,[4] revealing its molecular seesaw geometry (C_{2v}), which is in accord with the VSEPR model. Vibrational spectra of liquid SF_4 have also been assigned in terms of molecular C_{2v} point symmetry.[5] Sulfur tetrafluoride is one of the typical examples for a fluxional trigonal bipyramidal geometry, with rapidly exchanging axial and equatorial fluorine environments on the NMR timescale at room temperature.[6] At low temperature, the exchange can be slowed down, allowing the observation of two triplets in the ^{19}F NMR spectrum. The exchange of axial and equatorial fluorine environments of pure SF_4 has been shown to proceed by Berry pseudorotation with activation energies of 11.9 (gas phase) and 11.2 (liquid, solution) kcal mol^{-1}.[6] An NMR study of the temperature dependence of the ^{19}F NMR chemical shifts and ^2J coupling constants suggested the presence of labile fluorine bridging, with the possibility of dimer or chain formation being discussed.[7] Solid-state Raman spectroscopic data have been interpreted in terms of three different polymorphs, suggesting fluorine-bridged chains for the solid-state structure of SF_4.[8] Using miniature zone-melting techniques, the crystal structure of SF_4 has been reported to be severely disordered, and no discernible structure could be determined.[9] Despite the broad interest in the structure of SF_4, its solid-state structure has remained elusive as a consequence of its low melting point and highly reactive nature. The crystal structures of SeF_4 and TeF_4, on the other hand, have previously been obtained.[10] Tellurium tetrafluoride exists as TeF_3^+ units bridged by two fluoride ions, whereas SeF_4 contains distinct disphenoidal SeF_4 units, having Se···F contacts to two adjacent SeF_4 molecules.

Herein, we were able to obtain crystals of SF_4, which has a melting point of −121 °C, using two different methods: a) by slow cooling of neat liquid SF_4; and b) by crystallization from CF_2Cl_2 solvent. Both types of crystals were mounted at −145 °C and were shown to have the same unit cell. The initial data suggested a tetragonal unit cell. The correct structural solution, however, showed that SF_4 is twinned and crystallized in the orthorhombic system with two crystallographically unique ordered SF_4 molecules in the asymmetric unit (Figure 1). In our study, we did not find any evidence for a polymorph of SF_4.

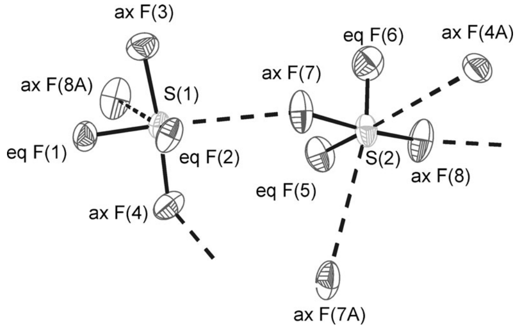

Figure 1. Thermal ellipsoid plot of SF_4. Ellipsoids are set at 50% probability. Selected bond lengths [Å], contacts [Å], and angles [°]: S1–F1 1.527(4), S1–F2 1.535(4), S1–F3 1.647(5), S1–F4 1.676(5); F1-S1-F2 101.0(2), F3-S1-F4 172.6(3), S1···F7 2.954(5), S1···F8A 3.031(5), F7···S1···F8A 121.2(2); S2–F5 1.553(4), S2–F6 1.474(6), S2–F7 1.671(5), S2–F8 1.635(4); F5-S2-F6 99.6(3), F7-S2-F8 171.6(3); S2···F4A 2.975(4), S2···F7A 3.261(6), F4A···S2···F7A 116.2(1).

The geometry of the SF_4 molecules agrees well with the seesaw geometry found for the gas phase.[3,4] The axial S–F bonds are longer (1.635(4)–1.671(5) Å) and more ionic in nature than the shorter equatorial S–F bonds (1.474(6)–1.553(4) Å). The axial and equatorial F-S-F angles found in the solid-state structure are indistinguishable from those of the gas-phase structure. The extended structure can be described as a three-dimensional network of SF_4 molecules linked by two weak intermolecular S···F contacts per SF_4 molecule. The shortest S···F contact found in the structure is 2.954(5) Å, which is shorter than the sum of the van-der-Waals radii (3.27 Å).[11] These contacts are exclusively formed by the more ionic axial fluorine atoms to the sulfur atoms of adjacent SF_4 molecules. None of the equatorial fluorine atoms form significant intermolecular contacts. This agrees very well with the more covalent nature of the S–F_{eq} bonds and the lower fluorobasicity of the equatorial fluorine atoms compared to the axial fluorine atoms. Because of the location of the lone pair in the F_{eq}-S-F_{eq} plane, the F···S···F angles (121.2(2)° and 116.2(1)°) are significantly larger than the F_{eq}-S-F_{eq} angles (101.0(2)° and 99.6(3)°). The weakness of the contacts is reflected in the low freezing point of SF_4 and the fact that the gas-phase and solid-phase metric parameters of the SF_4 molecule are the same within the experimental errors. The structures of SF_4 and SeF_4 are related in respect that both contain contacts between the axial fluorine atoms and the

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chalcogen atoms resulting in a fluorine-bridged network. In SF_4, however, only three of the four crystallographically different axial fluorine atoms form contacts, while in SeF_4 all axial fluorine atoms form Se−F⋯Se bridges.

A solid-state structural motif similar to that of neat SF_4 is observed in the crystal structure of the novel $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4[SF_5{}^-]\cdot 3\,SF_4$ salt. Excess SF_4 reacts with a mixture of water and 2,6-dimethylpyridine, yielding a white crystalline solid according to Equation (1). The $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4[SF_5{}^-]\cdot 3SF_4$ salt is stable up to −90 °C, above which temperature the crystals decompose.

$$6\,SF_4 + H_2O + 2\,N(C_5H_3)(CH_3)_2 \rightarrow [HNC_5H_3(CH_3)_2{}^+]_2F^- \cdots SF_4[SF_5{}^-]\cdot 3\,SF_4 + SOF_2 \qquad (1)$$

The asymmetric unit of $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4[SF_5{}^-]\cdot 3SF_4$ contains two 2,6-dimethylpyridinium cations that are hydrogen-bonded to a fluoride anion, an $SF_5{}^-$ anion (Figure 2), and four crystallographically different SF_4 molecules. Two different interaction modalities between F^- and SF_4 are present in this structure. The fluoride-ion acceptor properties of SF_4 towards F^- has been established by the formation of salts containing the $SF_5{}^-$ anion[12] and recently, the Lewis-acidity of SF_4 towards organic bases has conclusively been shown for the base $N(C_2H_5)_3$.[13]

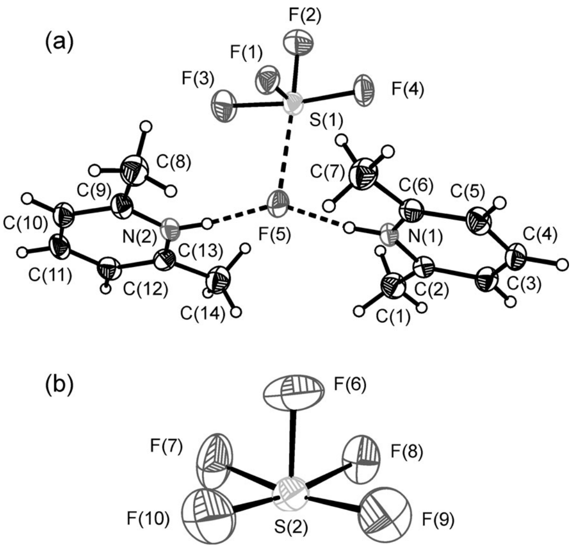

Figure 2. Thermal ellipsoid plot of a) the $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4$ moiety and b) the $SF_5{}^-$ anion in $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4[SF_5{}^-]\cdot 3SF_4$. Ellipsoids are set at 50% probability. Selected bond lengths [Å], contacts [Å], and angles [°]: S1–F1 1.545(2), S1–F2 1.549(2), S1–F3 1.650(2), S1–F4 1.706(2); S1⋯F5 2.487(2), F5⋯N1 2.554(3), F5⋯N2 2.553(3); S2–F6 1.564(2), S2–F7 1.730(2), S2–F8 1.763(2), S2–F9 1.719(2), S2–F10 1.664(2); F7-S2-F9 171.08(13), F8-S2-F10 170.70(13).

In the present structure, the fluoride which is hydrogen-bonded to two 2,6-dimethylpyridinium cations forms F⋯S1 contacts (2.487(2) Å) with one SF_4 molecule. These contacts are significantly stronger than the F⋯S contacts found in solid SF_4, resulting in an increase of the average S−F bond lengths in the $F^-\cdots SF_4$ moiety. The effect of coordination of fluoride on the structure of SF_4 in this salt is however less pronounced than that of $N(C_2H_5)_3$ coordination observed in the structure of $SF_4\cdot N(C_2H_5)_3$,[13] reflecting the weaker interaction between SF_4 and a fluoride that is hydrogen-bonded to two cations. A second significantly weaker interaction between sulfur and a fluorine atom from the $SF_5{}^-$ anion expands the coordination environment about S1 to six. The second fluoride ion in the structure is sufficiently naked to form the $SF_5{}^-$ anion, which adopts the expected square pyramidal structure. Apart from $Rb[SF_5]$, $Cs_6[SF_5]_4[HF_2]_2$,[12d] and $[Cs([18]crown\text{-}6)_2][SF_5]$,[12e] this is the fourth structurally characterized salt containing the $SF_5{}^-$ anion. Because three of the four equatorial fluorine atoms of this anion form F⋯S contacts, the anion is locked into one position without being disordered. As a consequence of the contacts, the anion geometry deviates from an idealized square pyramid. As expected, the axial S−F bond (1.564(2) Å) is much shorter than the equatorial S−F bonds (1.664(2) to 1.763(2) Å). The three equatorial fluorine atoms that have contacts to adjacent SF_4 molecules have significantly longer S−F bonds (1.719(2)–1.763(2) Å) than the bond to the other equatorial fluorine, which does not form contacts. The average of the equatorial S−F bond lengths is 1.719 Å, which is in excellent agreement with the average equatorial bond length reported for $Rb[SF_5]$ (1.718 Å). Moreover, the average of each pair of equatorial S−F bond lengths that are *trans* to each other gives this value within the experimental error. The fluorine in $SF_5{}^-$ that forms the strongest contact, that is, F8, has the longest and most ionic S−F bond and is trans to the shortest most covalent equatorial bond, that is, S2−F10. As mentioned for the anion in $Rb[SF_5]$,[12d] the presence of the lone pair on sulfur results in sulfur being 0.136 Å below the plane formed by the four equatorial fluorine atoms.

The packing of $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4[SF_5{}^-]\cdot 3\,SF_4$ shows two distinct layers along the *ab* plane. The SF_4 molecule that exhibits S⋯F contacts to the fluoride is located within a layer of the $[HNC_5H_3(CH_3)_2{}^+]$ cations and the F^- and $SF_5{}^-$ anions. The other three SF_4 molecules form a layer separating two ionic layers (Figure 3). The two types of SF_4 molecules show significant differences in the size of their fluorine atom ellipsoids, that is, the SF_4 coordinated to F^- exhibits smaller thermal parameters than the fluorine atoms of the free SF_4, reflecting significantly more thermal motion. This is paralleled by the relatively large thermal ellipsoids found in solid SF_4 at −173 °C. The coordination environments about sulfur in all SF_4 molecules include two S⋯F contacts (Supporting Information, Figure S3), which is similar to the coordination environment found in solid neat SF_4. The contacts involving fluorine atoms from the $SF_5{}^-$ anion (2.755(2) to 2.937(2) Å) are in general shorter than those from fluorine atoms of adjacent SF_4 molecules (2.867(2) to 3.164(3) Å), reflecting the larger fluorobasicity of the anions. The $F_4S\cdots FSF_3$ contacts are similar to those found in the structure of neat SF_4. As shown in Figure 3, the SF_4 molecules in the layer form contacts to molecules within the layer, as well as to the adjacent ionic layers, holding the layers together.

The Raman spectrum of solid SF_4 exhibits significant splitting as previously observed.[8] These splittings can be

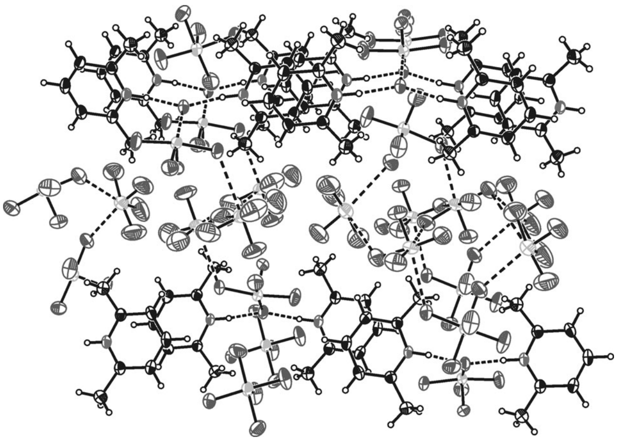

Figure 3. Thermal ellipsoid view along the *a* axis of the packing of $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3SF_4$. Ellipsoids are set at 50% probability.

explained by the presence of two crystallographically different SF_4 molecules and/or by vibrational coupling between SF_4 molecules in one unit cell. The Raman spectrum of $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3\,SF_4$ at −100 °C is depicted in Figure 4 and contains the characteristic signals associated with the $HNC_5H_3(CH_3)_2{}^+$ cation and the $SF_5{}^-$ anion. The latter were assigned based on the vibrational assignments previously reported for the Cs^+ and $[Cs([18]crown\text{-}6)_2]^+$ salts.[12] The Raman spectrum also shows several bands attributable to SF_4. Interestingly, two sets of bands in the equatorial SF_2 stretching region can be distinguished and tentatively assigned to $\nu_s(SF_{2,eq})$ of SF_4 in the layer (880 cm^{-1}), which is close to that of neat solid SF_4 (888, 879 cm^{-1}), and that of SF_4 coordinated by F^- (863 cm^{-1}; Supporting Information, Table S1). A Raman spectrum of solid $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3\,SF_4$ recorded at −85 °C contains a broadened signal at 884 cm^{-1}, which resembles the broad signal observed in liquid SF_4. This observation corroborates the observation of significant thermal motion within the SF_4 layer and suggests the onset of decomposition via release of SF_4.

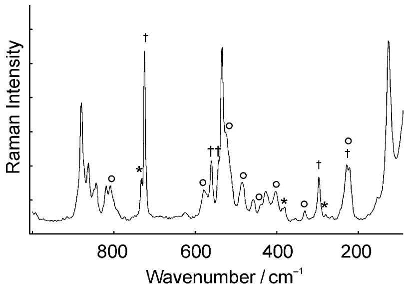

Figure 4. Raman spectrum of $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3\,SF_4$ at −100 °C. Asterisks (*) denote bands arising from the FEP sample tube. Bands attributed to the 2,6-dimethylpyridinium cation and to the $SF_5{}^-$ anion are denoted by (†) and (○), respectively.

In conclusion, the structure of SF_4 in the solid state has been elucidated for the first time. The structure can best be described as a network with weak intermolecular S···F contacts formed exclusively with the axial fluorine atoms that exhibit more ionic character. The structure is different from previous predictions of chain-type or dimeric structures.[7] A similar structural motif is found in the novel $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3\,SF_4$ salt which contain SF_4 layers. As in neat SF_4, the SF_4 molecules within the layer of the salt have two S···F contacts of similar distances and do not form distinct dimers or chains. Because of the weakness of interactions, the overall structure, that is, network versus layer, greatly depends on the nature of composition of the compound. The $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3\,SF_4$ salt is the first compound that contains a range of interaction motifs between SF_4 and F, that is, $F_4S{-}F^-$ (1.564(2) to 1.763(2) Å), $F_4S{\cdots}F^-$ (2.587(2) Å), $F_4S{\cdots}FSF_4{}^-$(1.755(2) to 2.937(2) Å), and $F_4S{\cdots}FSF_3$ (2.867(2) to 3.164(2) Å).

Experimental Section

All volatile materials were handled on a vacuum line constructed of nickel, stainless steel, and FEP. Reaction vessels were fabricated from FEP tubing (¼-in (0.635 cm) o.d.) and outfitted with Kel-F valves. All reaction vessels were rigorously dried under dynamic vacuum followed by treatment with more than 1 atm of F_2 gas.

Sulfur tetrafluoride (Ozark-Mahoning Co.) was purified by passing the gas through a column of activated charcoal. Traces of thionyl fluoride and sulfur hexafluoride were present in the sulfur tetrafluoride, but did not interfere with the chemistry. Difluorodichloromethane (Synquest Labs Inc.), 2,6-dimethylpyridine (Sigma–Aldrich) were used as received.

$[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3\,SF_4$: Water (0.016 g, 0.89 mmol) was injected into a ¼-in. FEP reactor equipped with a Kel-F valve using a micro syringe. 2,6-dimethylpyridine (0.176 g, 1.64 mmol) was then injected into the ¼-in. FEP reactor in a dry nitrogen filled glove bag. A large excess of SF_4 was vacuum-distilled onto the frozen mixture at −196 °C. Upon melting of SF_4 at −120 °C, a vigorous reaction occurred, causing a white insoluble precipitate to form. Warming the reaction mixture to 0 °C formed a clear colorless solution. Upon cooling of this solution to −85 °C large needles formed. Excess SF_4 was partially removed under dynamic vacuum at −95 °C, yielding 0.691 g of a white solid, namely $[HNC_5H_3(CH_3)_2{}^+]_2F^-{\cdots}SF_4[SF_5{}^-]{\cdot}3SF_4$ with small amounts of residual SF_4.

Raman spectra were recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen cooled Ge detector, and R-496 temperature accessory. The actual usable Stokes range was 50 to 3500 cm^{-1}. The 1064-nm line of an Nd:YAG laser was used for excitation of the sample. The Raman spectra were recorded at −110 °C with a spectral resolution of 2 cm^{-1} using laser powers of 300 mW.

X-ray crystallography: SF_4, formula weight $M_r = 108.06\,g\,cm^{-3}$, clear colorless plate ($0.17\times0.15\times0.14\,mm^3$), orthorhombic, $P2_12_12_1$, $Z=8$, $a=6.773(4)$, $b=6.812(4)$, $c=13.122(8)$ Å, $V=605.5(6)$ Å^3, $\rho_{calcd}=2.371\,g\,cm^{-3}$, $2\theta_{max}$ 54.4°, $\lambda(Mo_{K\alpha})=0.71073$ Å, 100(2) K, 6874 reflections, 1387 unique reflections ($R_{int}=0.052$), absorption coefficient ($\mu=0.98\,mm^{-1}$), $R_1=0.050$, $wR_2=0.112$.

$C_{14}H_{20}F_{22}N_2S_5$: formula weight $M_r=794.61\,g\,cm^{-3}$, clear colorless block ($0.16\times0.19\times0.57\,mm^3$), orthorhombic, $P2_12_12_1$, $Z=4$, $a=7.4597(10)$, $b=18.150(2)$, $c=21.863(3)$ Å, $V=2960.2(7)$ Å^3, $\rho_{calcd}=1.783\,g\,cm^{-3}$, $2\theta_{max}=55.2°$, $\lambda(Mo_{K\alpha})=0.71073$ Å, 133(2) K, 33934 reflections, 6819 unique reflections ($R_{int}=0.033$), absorption coefficient ($\mu=0.54\,mm^{-1}$), $R_1=0.042$, $wR_2=0.117$.

The crystals were mounted at low temperature under a stream of cold dry nitrogen as previously described.[14] The crystals were centered on a Bruker SMART APEX II diffractometer, controlled by the APEX2 Graphical User Interfact software.[15] The program SADABS[16] was used for scaling of diffraction data, the application of a decay correction, and a multi-scan absorption correction. The program SHELXS-97[17] was used for both solution and refinement. A structure solution was obtained by direct methods. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-425996 (SF_4). CCDC 932409 ($C_{14}H_{20}F_{22}N_2S_5$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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